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Dissolution of electrically inactive phosphorus by low temperature annealing

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Abstract

In this study we investigate the dissolution of electrically inactive phosphorus complexes by low temperature annealing after the $POCl_3$ diffusion process. This has the immediate consequence that the existing near-surface emitter volume SRH recombination can be reduced. Thereby, a significant reduction of emitter saturation current density j_{0E} is achieved without driving the emitter further into the silicon substrate. For short-term temperature treatments well below the $POCl_3$ diffusion temperature, a reduction of up to -60 fA/cm² has been achieved. This study increases our understanding of the formation and dissolution of electrically inactive phosphorus complexes during post-annealing processes.

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Keywords: low-temperature annealing; electrically inactive phosphorus; $POCl_3$ diffusion

1. Introduction

Today, most screen printed solar cells have highly doped emitters which include a non-negligible fraction of electrically inactive phosphorus on the emitter surface [1]. Here, one must distinguish between stable P-precipitates and less stable complex phosphorus-oxygen structures. Furthermore, it can be assumed that Shockley-Read-Hall (SRH) recombination in the near surface emitter region is strongly correlated with the density of these electrically inactive P complex structures [2].

The formation of the electrically inactive phosphorus depends on various process parameters such as $POCl_3$-N_2 gas flow, process temperature as well as the cooling-down phase. In a conventional diffusion process very high cooling ramps (>20 K/s) are usually used. Thereby, we assume that during the rapid cooling down phase P-

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complexes from the surface of the phosphorus silicate glass and the silicon surface transfer into a frozen state by the quenching effect [3]. In this study, we introduce an additional low temperature annealing (LTA) to reverse this effect and thereby dissolve a significant part of the electrically-inactive phosphorus on the emitter surface and in the near surface emitter region [4-10].

2. Experimental details

2.1. Interaction between the density of the electrically-inactive P and LTA

In the first experiment 3 different $POCl_3$ diffusions have been processed to form 3 emitter structures with very high, medium and very low density of electrically inactive phosphorus. For this experiment, FZ silicon wafers of 200 µm thickness and a resistivity of 2 & 200 Ωcm were used. After the diffusion process, the wafers were divided into 2 groups, with and without PSG, followed by 3 LTA steps. After this process, all samples were cleaned by a conventional cleaning procedure (H_2O-HCl-HF) and symmetrically passivated by PECVD SiN_x (including firing). The samples were finally characterized. We intend with this first experiment to show the temperature range in which LTA exerts the strongest influence on the inactive P-concentration. In the second experiment, the density of the inactive phosphorus was reduced by steps using a wet-chemical emitter etch-back procedure EEB [11]. Thereby we start with an emitter with a high density of electrically-inactive phosphorus. The wet chemical EEB allows to etch-back the emitter homogeneously in small nm steps. The focus is thereby on showing the extent to which the density of the inactive phosphorus can be influenced or respectively reduced by LTA in a defined temperature range.

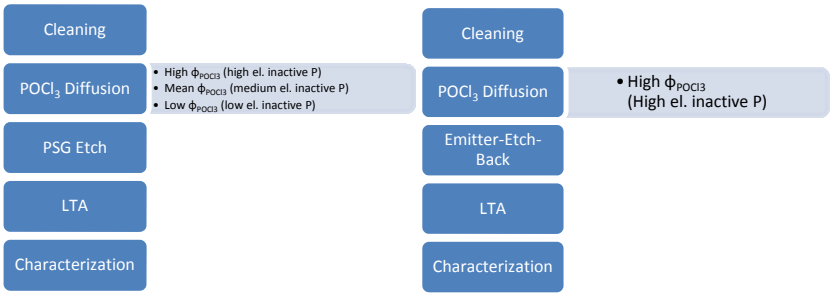

Fig. 1. Experimental details of the studies on the influence of LTA on the P-concentration and the recombination activity of the n-type emitter

3. Results and discussion

3.1. Temperature range of LTA

In the first experiment, the influence of the temperature range on the change in electrically active and inactive P is shown. Measured sheet resistances as a function of LTA temperature is displayed in Fig. 2 (left). Since sheet resistance is determined by the density of electrically active P in the emitter, here we can analyze the influence of LTA on electrically active P in dependency on LTA temperature. Two emitter structures with lower and higher densities of electrically inactive phosphorus are studied. In Fig. 2 we see that LTA leads to a weak increase in emitter sheet resistance. The change of emitter sheet resistance appears here for both types of emitters. The absolute change in R_{sheet} is <2.8 Ωcm and is therefore insignificant. Since LTA temperatures studied in this investigation lie far below the diffusion temperatures, we assume that LTA causes a restructuring of the P-O complexes on the emitter surface and in the emitter volume. Fig. 2 (left) shows furthermore that LTA temperature has only a small influence on sheet resistance of the emitter. Comparison of ECV profiles as a function of LTA temperature range in Fig. 2 (right) shows that LTA temperature far below 800°C has only a very weak influence on the change of the electrically active P.

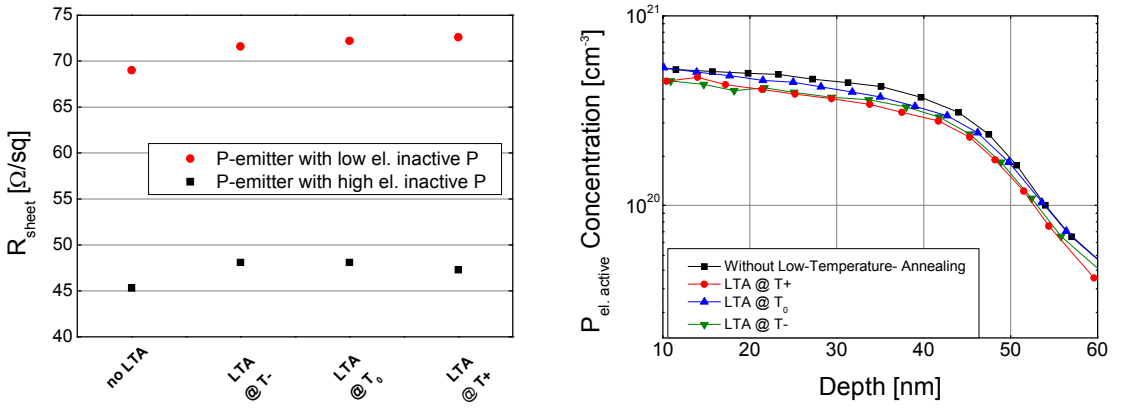

Fig. 2. (left) Measurements of emitter sheet resistance as a function of the LTA temperature for 2 n-type emitters containing high and low density of electrically inactive P. (right) Comparison of electrically active P concentration profiles for different LTA temperature ranges.

3.2. Emitter saturation current density after LTA process

The goal of the LTA process is to change the density of electrically inactive P at temperatures far below the usual $POCl_3$ diffusion temperature. Fig. 3 (left) shows j_{0E} values for three different emitter structures, measured using QSSPC, which display different densities of electrically inactive P. The effect of the LTA process is largest with Emitter A (high electrically inactive P concentration). The reduction of j_{0E} can here be attributed to a reduction of SRH recombination, since with the LTA process no significant change could be determined in emitter sheet resistance. With decreasing density of electrically inactive phosphorus (Emitters B & C), the reduction in j_{0E} decreases. With Emitter C, with hardly any electrically inactive P, no reduction in j_{0E} due to the LTA process is measured. In Fig. 3 (right) we see the electrically active P juxtaposed with the electrically inactive P of the here studied emitter structures. The reduced influence of the LTA process for Emitter C (blue lines) can be attributed to the identical concentration of the electrically active and the total P concentration.

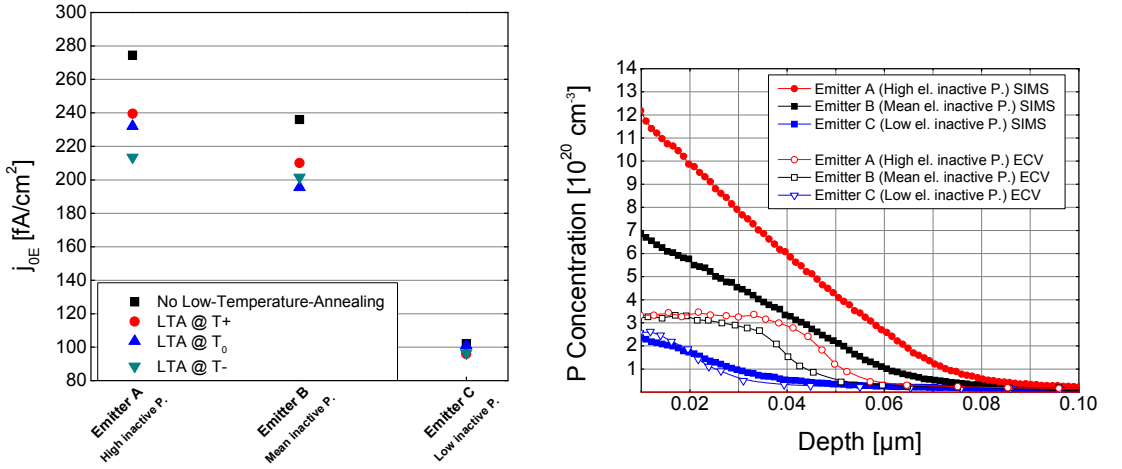

Fig. 3. (left) Influence of LTA on 3 different emitters for 3 different annealing temperatures. (right) Juxtaposition of the ECV and SIMS P-profiles of the here studied emitters A, B & C.

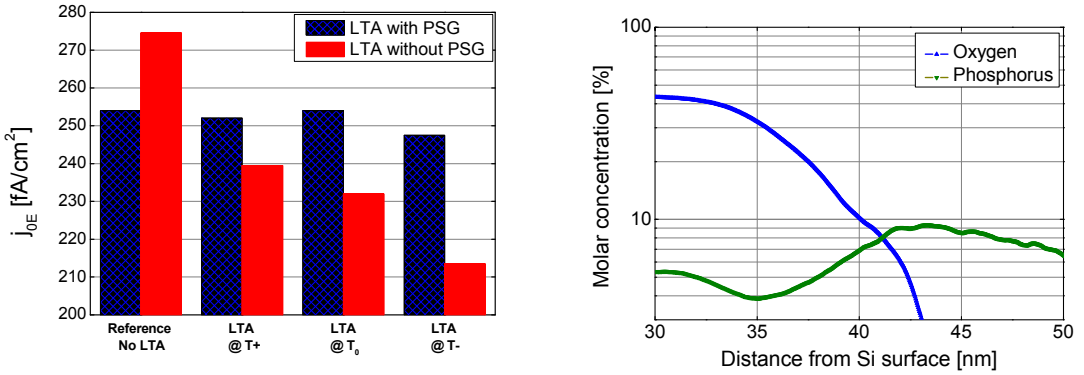

Fig. 4. (left) Comparison of j_{0E} measurements of Emitter A (high electrically inactive P) after 3 LTA processes. The LTA processes with PSG show no change in emitter passivation. (right) Measurements of P and O in the PSG region by optical emission spectroscopy.

As already shown in Fig. 3 (left), at temperatures well below the diffusion temperature the LTA process reduces the recombination activity of emitters that display a high density of electrically inactive P. The LTA process with the lowest post annealing temperature T- shows the most significant reduction of j_{0E} ($\Delta j_{0E} \approx$ -60 fA/cm²). In case of presence of PSG during LTA, no change in emitter recombination activity was determined. Here we assume a dissolution of less stable, but nevertheless recombination active P-O complexes on the surface and in the surface-near emitter region. From earlier studies we know that with an emitter such as studied in Fig. 4 (left), the PSG is a multi-layer system and the interface to silicon displays an above-average concentration of P-O clusters. We assume here that through the LTA process there is an increased diffusivity of P-O molecules from the PSG in the direction of the silicon surface. This mechanism would compensate for any changes in the electrically inactive P on the emitter surface. Therefore, the PSG could here, despite low LTA temperatures, still be viewed as an active source layer of P.

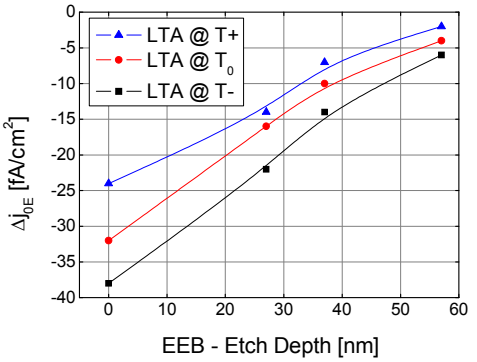

Fig. 5. LTA process on several etch-back emitters. The j_{0E} measurements show that the efficiency of LTA is reduced in case of an etch-back emitter with very low density of electrically inactive P (lines are guides to the eye).

To find out how efficient the LTA process is, in the last experiment an emitter with high density of electrically inactive P is step-by-step etched-back by means of the wet-chemical EEB method. After the emitter etch-back, samples were cleaned and dielectrically passivated on both sides by means of PECVD SiN_x (including firing). The change of j_{0E} in Fig. 5 is determined from the difference between j_{0E} of an LTA-free process and j_{0E} after the LTA process. We see that the reduction in j_{0E} and thereby the reduction of the emitter's recombination activity decreases with increasing etch depth. The explanation is that here step-by-step the emitter and thereby also the electrically inactive P was etched-back. The efficiency of the LTA process increases here as before with falling temperature.

4. Conclusion

In this study we have dealt with the effect of a low temperature annealing (LTA) process after $POCl_3$ diffusion processes and could detect a significant influence on the density of the electrically inactive P in the emitter. We assume that the LTA process leads to dissolution of less stable P-O complexes in the near-surface region. The reduction of electrically inactive P caused by the LTA process has direct influence on the emitter's recombination activity. Measurements of emitter saturation current density on different emitter structures with and without LTA process confirmed this hypothesis. The fact that the LTA process appears to have no particular influence on the electrically active P concentration can likewise be explained by low process temperatures, well below the usual diffusion temperatures. In case of the presence of a highly doped PSG layer during the LTA process, no change in j_{0E} could be detected. This fact indirectly shows that the PSG layer can also be regarded as an active layer at low process temperatures. In this case, less as a source layer for the electrically active P concentration in the emitter, but rather more as a source layer for the diffusion of P-O clusters from the PSG on the silicon surface. The LTA process can without hesitation be integrated into the process of manufacturing solar cells, whereby this process can also be very well integrated in the arrays of low temperature gettering [12, 13].

Acknowledgements

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